

TPS:HA  
V-3

U. S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS  
WASHINGTON

Letter  
Circular  
LC-538

(December 2, 1938)

Replaces LC-455

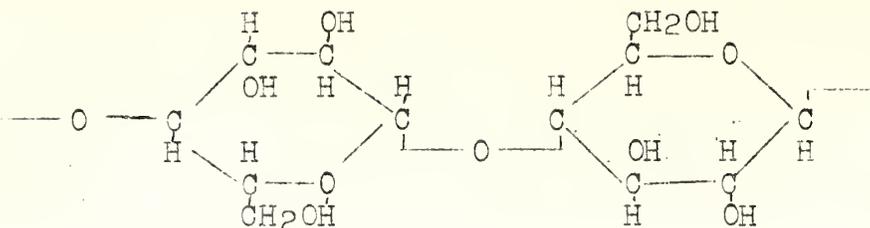
TRANSPARENT WRAPPING MATERIALS

The use of transparent wrapping materials for the packaging of a host of commodities has become a familiar everyday experience. This has occasioned frequent inquiries regarding their composition and properties. In the descriptions of these materials which follow, an effort has been made to provide general information for the individual who may not be familiar with the technology of synthetic plastics. Many of the references in the bibliography have been chosen because they represent sources giving specific details regarding properties and applications. These materials are all patented. References to patents will be found in "Chemical Abstracts," published by the American Chemical Society. This journal is available in many public libraries and in the libraries of universities and technical schools.

The transparent wrapping materials discussed are continuous colloidal films and are thus distinct from paper which has been treated to render it semi-transparent. They belong to a group of substances which are not wholly synthetic but are the products of chemical alteration of materials occurring in nature, namely cellulose and rubber, the properties of which are partially retained.

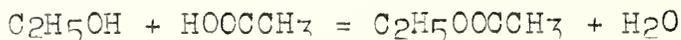
Cellulose Derivatives

The bulk of the transparent wrapping materials which are manufactured is composed of cellulose or its derivative, cellulose acetate. Cellulose is the principal building material of the cell walls of plants. Its chief sources are wood and cotton. To understand better the reactions involved, it is essential to bear in mind that in its reactions cellulose behaves like an alcohol. Alcohols are a group of organic compounds which are characterized by the existence in their molecules of what are known as hydroxyl groups. In structural formulas these are expressed as OH. Thus the commonly known ethyl alcohol is the hydroxy derivative of ethane and is expressed as  $C_2H_5OH$ . Chemically, cellulose is a polymer composed of recurring units of glucose anhydride ( $C_6H_7O_2(OH)_3$ ). One suggested formula for the cellulose molecule is the following:



It will be noted that each unit contains three hydroxyl groups, and hence it behaves in its reactions like a trihydric alcohol.

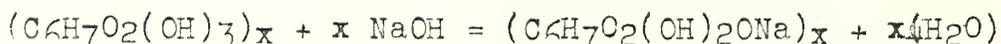
Among the typical reactions of alcohols is the formation of esters. A simple example of esterification is the reaction of ethyl alcohol and acetic acid which is expressed as:



Esterification is frequently employed in the preparation of cellulose derivatives. The two cellulose derivatives used in the manufacture of transparent wrapping materials are cellulose xanthate, which in the process of manufacture is regenerated to cellulose, and cellulose acetate.

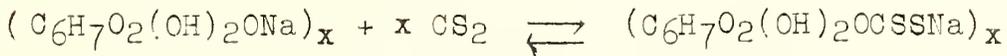
### Manufacture of Regenerated Cellulose

In the preparation of regenerated cellulose the first step is the treatment of wood pulp or cotton with a water solution of sodium hydroxide (caustic soda, lye). As the result of this treatment the fibers become translucent and swell and acquire a silky appearance. There is a difference of opinion in regard to the exact mechanism of the reaction which takes place. Whether or not a true chemical compound is formed is uncertain, but the product behaves in subsequent reactions in a manner characteristic of a true compound. Cross and Bevan represent the reaction between cellulose and sodium hydroxide, employing the empirical formula for cellulose, as:



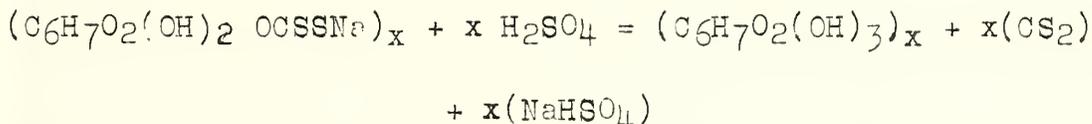
The product is thus regarded as a sodium alcoholate.

The cellulose is allowed to remain in contact with the solution of sodium hydroxide for a definite period of time at a definite temperature. The excess solution of alkali is then removed. The material is treated with carbon bisulfide. The reaction which takes place results in the formation of an orange-colored mass in which the fibrous character of the cellulose gradually disappears. This material is soluble in a dilute solution of sodium hydroxide. The resulting solution, which is of about the consistency of corn syrup, is known technically as viscose. The reaction which has taken place is presumed to be the formation of the sodium salt of cellulose xanthic acid and is represented as follows:



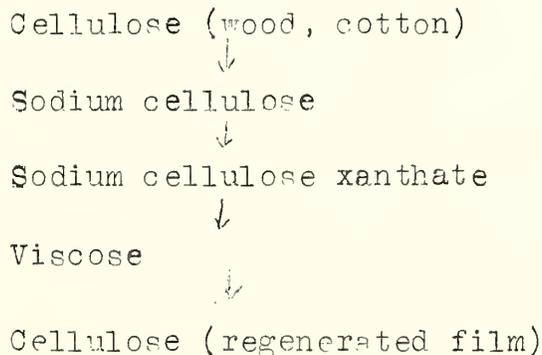
Viscose is an unstable substance and undergoes a series of reactions which are not clearly understood but which undoubtedly involve the formation of a more complex molecule. A number of side reactions also occur which yield a variety of substances. The changes which take place in viscose with time affect the coagulability, and the change in this property is closely observed during a period of "ripening." After this has proceeded a sufficient length of time, the viscose is ready for regeneration or conversion into film.

In the formation of the regenerated film of cellulose, the viscose is forced through a narrow slot and passes directly into a water solution which contains sulfuric acid and sodium sulfate. The regeneration which results takes place in two steps; first, the viscose is coagulated by the sodium sulfate and simultaneously the alkali is neutralized by the sulfuric acid; and second, the decomposition of the sodium cellulose xanthate is accomplished by the continued action of the excess sulfuric acid. The reaction with this acid results in the recovery of cellulose with the liberation of carbon bisulfide and the formation of sodium acid sulfate. The reaction is expressed as:



In the manufacture of regenerated cellulose in tubular form (cellulose sausage casings), the viscose is extruded into the acid solution as a seamless tube supported by a mandrel.

It is essential to remember that, practically, the chemical composition of regenerated cellulose is the same as that of raw cellulose. The process of manufacture may be represented as:



.. 11

After its precipitation the film passes over rolls into a bath of water to remove acid and salts, through a solution which may contain sodium hydroxide or sodium sulfite to remove residual sulfur, and through a bleaching bath containing sodium hypochlorite. This treatment is followed by further washing in water. The final step is bathing in a water solution of glycerol. The latter remains in the film after drying and imparts pliability to the finished film. The entire process from the coagulation of the viscose to the finished film is continuous and progressive.

Wrapping material composed of regenerated cellulose is marketed in this country under the trade names of Cellophane, Primophan, Sylphrap, and Tee-Pak.

### Chemical and Physical Properties of Regenerated Cellulose

Regenerated cellulose displays all the properties of cellulose. It swells in a solution of sodium hydroxide, and is hygroscopic. It undergoes all of the typical cellulose reactions such as the formation of the nitrate, acetate, ethyl ether, and xanthate. It can not be dissolved in organic solvents. In this respect it differs from cellulose nitrate and cellulose acetate, which are employed in lacquers and plastics. Like cellulose it can be dissolved in copper ammonium hydroxide (Schweitzer's reagent) as well as in a number of strong organic bases.

Regenerated cellulose film has considerable tensile strength but very low resistance to tear. The tensile strength is greatest in the direction of flow of the film during its manufacture. The weight required to break a strip 1.62 inch wide and 0.001 inch thick is stated to be about 15.7 lbs. in the longitudinal direction and 7.3 lbs. in the transverse direction.

Films of regenerated cellulose are practically impermeable to hydrogen and helium. They readily allow the passage of water vapor, and toward water solutions they behave as dialyzing membranes, permitting the separation of substances of varying molecular size. In the presence of moisture, water-soluble gases, such as oxygen and carbon dioxide, readily penetrate the material. Perfectly dry film is stated to be impermeable to all gases.

The transparency of regenerated cellulose to light waves in the therapeutic region, 2900A to 3100A, is stated to be about 70 percent. It has been suggested as a window material in the treatment of diseases by heliotherapy since it does not lose a great deal of its transparency upon prolonged exposure to ultraviolet light. The material is not, however, weatherproof.

### Moisture-Proofed Wrapping

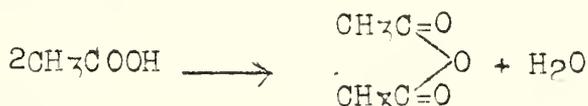
For a great many packaging purposes, notably food stuffs, it is desirable that the passage of moisture through the film be prevented as much as possible. To render the film moisture-resistant it is the practice to coat it with a lacquer, containing cellulose nitrate, and frequently waxes, gums, resins, and plasticizers. Upon evaporation of the solvent, the surface is coated on both sides with a thin film which is less permeable to moisture than the uncoated cellulose film.

### Adhesives

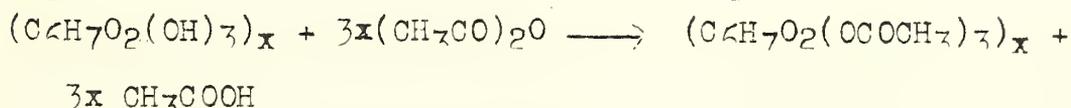
Fabrication of regenerated cellulose film into articles and the sealing of packages require the use of an adhesive. For material which has not been moisture-proofed, water-soluble adhesives such as animal glue, are employed where a strong bond is desired. For use on moisture-proofed material it is essential to use a material which will adhere to the lacquered surface. For this purpose adhesives containing a cellulose nitrate base are employed. In many cases it is customary to moisten the surfaces to be sealed with a solvent for the moisture-proofing lacquer. A solvent such as methyl cellosolve is applied to the surface to be sealed during the machine-folding operation. A slight softening takes place, and, when the edges are pressed together, and the solvent is subsequently evaporated by passing the wrapped package over hot plates, adhesion occurs.

### Cellulose Acetate

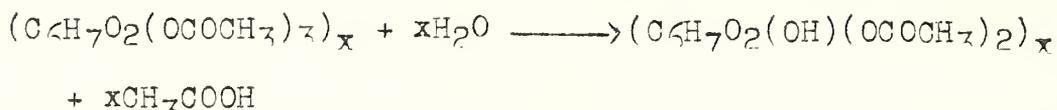
Cellulose acetate is the cellulose ester of acetic acid and like regenerated cellulose, it can be produced in the form of thin, transparent film. It is prepared by treating raw cellulose with acetic anhydride in the presence of acetic acid and a small amount of sulfuric acid which behaves as a so-called catalyst. Acetic anhydride is a liquid which in substance represents the product obtained when one molecule of water is eliminated from two molecules of acetic acid, a process which may be represented as:



Acetic anhydride reacts readily with alcohols to form esters. The primary reaction in the acetylation of cellulose may be represented by the following equation:



The preparation of commercial types of cellulose acetate involves approximately complete esterification to the cellulose triacetate. The triacetate does not have the desired qualities for numerous purposes and, particularly, it is not soluble in a wide range of convenient solvents. To obtain a satisfactory product, it is necessary to subject the material to a mild hydrolysis which replaces one or more acetyl groups with hydroxyl groups. The reaction in the case of the removal of one acetyl group is:



The cellulose diacetate shown above does not represent the precise formula of the product usually obtained, which is likely to be a mixture of hydroacetates representing varying degrees of acetylation.

The resulting product is suitable for a variety of purposes, including the production of molded plastics and film. In the form of thin film it is produced by a method known as a casting process. The cellulose acetate, together with a definite amount of plasticizer, is dissolved in a suitable volatile solvent. The purpose of the plasticizer, usually a liquid having a very low vapor pressure, is to impart flexibility to the film. The cellulose acetate solution is permitted to flow in a carefully regulated stream onto the polished surface of a large metal drum. The drum is revolved in a chamber in which the atmospheric conditions are regulated and a means is provided for the constant removal and recovery of solvent. The dried film deposited upon the drum is then removed in the form of a continuous sheet.

Transparent wrapping material, a compound of cellulose acetate, is marketed under the trade names of Kodapak and Protectoid.

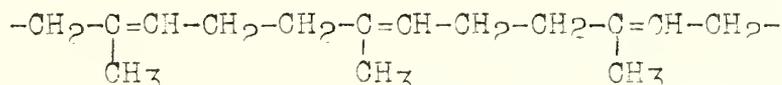
#### Properties of Cellulose Acetate

Cellulose acetate differs from regenerated cellulose in that it is thermoplastic, that is, it softens when heated and regains its normal condition upon cooling. It is also soluble in numerous solvents such as acetone, methyl acetate, diacetone alcohol, methyl cellosolve, as well as two-type solvents such as mixtures of ethylene chloride and alcohol. Cellulose acetate is much less hygroscopic and consequently more water resistant than cellulose. The material ignites at a comparatively high temperature and burns slowly. Clear, colorless films are capable of transmitting as much as 80 to 90 percent of the visible light. The solubility of the film in organic solvents and its thermoplasticity render it capable of being cemented securely to itself as well as to paper and box-board.

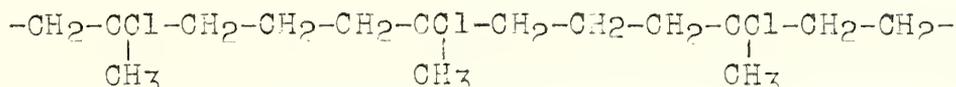
Cellulose acetate wrapping is available in roll or sheet form in thicknesses of 0.00083 to 0.002 inch.

### Rubber Hydrochloride

It is customary to consider the structure of natural rubber as consisting of long chains containing the recurrent units of isoprene. It has been suggested that rubber has a linear polymeric structure expressed as:



rubber reacts with hydrogen chloride the product obtained presumably being represented by the following:



The reaction doubtless involves not only the combination of the rubber with the hydrogen chloride but also a change in the structure of the rubber molecule as a whole, a condition which cannot be expressed in structural form. Rubber hydrochloride differs from the unreacted rubber in its physical properties notably in the reduction of its elastic extensibility.

Combining rubber with hydrogen chloride can be accomplished by saturating a solution of rubber, in benzene or chloroform, with hydrogen chloride. The product is then recovered as a precipitate of the rubber hydrochloride by the addition of alcohol to the solution. Another method of preparation consists in suspending thin sheets of rubber in ethyl acetate which has been saturated with hydrogen chloride. Rubber merely swells and does not go into solution in ethyl acetate. After several hours' time the rubber which has reacted with the hydrogen chloride is removed in sheet form.

Details of the manufacture of thin films of rubber hydrochloride for wrapping purposes are not available. Since the material is soluble in solvents such as benzene, a method of casting the film upon a metal base might be employed.

## Properties of Rubber Hydrochloride

Thin sheets of rubber hydrochloride resemble in their appearance and "feel" those of other transparent wrappings. Their tensile strength is stated to be less, but this is compensated by their greater elasticity and resistance to tear. When heated, rubber hydrochloride becomes ductile and plastic. Rubber hydrochloride is highly resistant to moisture and because of this quality it has been extensively employed in the fabrication of umbrellas, raincoats, and garment bags. It is also more resistant to the action of acids, gasoline, and oils than is rubber. It is soluble in benzene and chloroform but not in alcohol or ether. It burns with difficulty. For most packaging purposes the material is employed without the addition of a plasticizer. For such uses as garments a plasticizer is included.

Sealing the film may be accomplished by heating the material at temperatures between 220° and 250°F, or an adhesive containing rubber hydrochloride in solution may be used.

The material, in thicknesses ranging from 0.001 to 0.0025 inch, is marketed under the trade name of Pliofilm.

## Identification of Type of Film

If the nature of a sample of transparent wrapping is not definitely known, the following simple tests are believed to be sufficiently discriminative to afford identification of any of the three materials mentioned in this circular.

Behavior on Ignition.— When the flame from a burning match is applied to the edge of a small piece of the film, the rate of burning and the nature of the burned residue are indicative of its composition.

If the film is composed of regenerated cellulose and the surface has not been coated with moisture-proofing, it will burn with about the rapidity of newsprint. The moisture-proofed type, which will doubtless be more frequently encountered, will tend to flare up with momentary violence because of the inflammable nature of the cellulose nitrate coating. The edge of the burned portion of film will resemble that of burned paper. If the material is composed of cellulose acetate, the rate of burning will be somewhat slower than that of paper. As burning proceeds, the edge will tend to melt and not be completely consumed. Small charred globules will gather along the edge and may even drop off as burning progresses.

Rubber hydrochloride will melt and behave much like cellulose acetate when exposed to the flame. Combustion will tend to cease, however, when the source of ignition is removed. It is characteristic of organic compounds, which contain substantial amounts of chlorine in the molecule, that they burn with difficulty.

An odor resembling that of burning feathers or similar animal matter indicates that the material is composed of a protein, such as gelatin or casein. Gelatin, particularly, is sometimes employed in the preparation of bottle seals, capsules, and color screens for theatrical lights.

Effect of Solvents.-- Small specimens of the film are immersed in acetone and in benzene, and, after standing for some time or after the solvents have been gently heated (not over a free flame) for a short while, the condition of the immersed film is observed. If the film remains unchanged in either solvent, it is conclusive evidence that the material is regenerated cellulose. If it is completely dissolved by the acetone and unaffected by benzene, it is presumably cellulose acetate. If it is merely slightly whitened by the acetone and completely dissolved in the benzene, it is highly probable that it is rubber hydrochloride.

Effect of Sulfuric Acid.-- Test specimens are immersed in a solution containing equal volumes of concentrated sulfuric acid and water. The solution is gently warmed. If the material is slowly dissolved to give a dark-colored, turbid solution which gives only a faint caramel-like odor, the film is presumably regenerated cellulose. If it dissolves to give a dark yellow solution, and, on continued heating, the odor of acetic acid can be detected, it is conclusive evidence that the material is cellulose acetate. If the film remains practically unattacked, aside from a slight darkening after the solution has been warmed for some time, it is indicative of rubber hydrochloride.

Bibliography

The following are some of the most readily available articles:

Regenerated Cellulose

- Anonymous. Cellophane. Fortune 5, 74-9, 96, 101-2 (1932).
- R. Bonar, F. Bonar, and E. C. H. Davies. Cellophane roll films for slide lanterns. J. Chemical Education 10, 92-4 (1933).
- W. H. Carothers. Polymerization. Chemical Reviews 8, 419 (1931).
- Frederick T. Carson. Permeability of membranes to water vapor with special reference to packaging materials. National Bureau of Standards Miscellaneous Publication M127 (1937).
- W. H. Charch and A. G. Scroggie. Determination of water-vapor permeability of cellulosic wrapping materials. Paper Trade Journal 101, 31-9 (1935).
- R. F. Conway. Chemistry of Cellulose Derivatives. Industrial Engineering Chemistry 30, 516-23 (1938).
- C. Doree. The Methods of cellulose chemistry (Chapman and Hall, Ltd., London, 1933).
- M. Halama. Transparent viscose films: their manufacture and uses. World's Paper Trade Review 97, 828-36, 894, 896 (1932).
- R. S. Hatch. Advances made in the manufacture of wood cellulose of high purity and its expanding uses for rayon, cellophane, plastics, etc. Paper Trade Journal 105, No. 4 28-9 (1937).
- Wm. F. Henderson, H. E. Dietrich. Cellulose sausage casings. Industrial Engineering Chemistry 18, 1190-94 (1926).
- E. Hubert. The preparation and properties of artificial sponges from cellulose. Kolloid-Zeitschrift 57, 253-58 (1931).
- W. H. Hyden. Manufacture and properties of regenerated cellulose films. Industrial and Engineering Chemistry 21, 405-10 (1929).
- W. B. Lee. Adhesives and adhesion. Some mechanical properties of materials and glued metal joints. Industrial and Engineering Chemistry 22, 778-80 (1930).

- J. W. McBain, S. S. Kistler. Membranes for high-pressure filtration. Transactions Faraday Society 26, 157-62 (1930).
- W. L. Morgan. Retarding rancidity. Colored transparent cellulosic wrappers. Industrial and Engineering Chemistry 27, 1287-90 (1935).
- R. S. Shutt, Edward Mack, Jr. The retention of glycerol and glycols by cellophane and cotton cellulose. Industrial and Engineering Chemistry 25, 687-92 (1933).
- B. H. Walden. Cellophane for lantern slides. Science 77, 91 (1933).
- K. L. Warren. Cellophane for lantern slides. Science 76, 573 (1932).
- Robert B. Withrow. Cellophane and gelatin filters for the ultraviolet. Bulletin Basic Science Research 3, 82-8 (1931).
- Ullmann. Enzyklopaedie der Technischen Chemie, 2nd Edition 3, 157-63.

#### Cellulose Acetate

- Anonymous. New wrapping material produced (Kodapak). Industrial and Engineering Chemistry 24, 324 (1932).
- J. Eggert. Cellulose acetate or viscose sheets? Nitro-cellulose 4, 141-2 (1933).
- G. J. Esselen. Modern developments in applied chemistry. Industrial and Engineering Chemistry 26, 26-30 (1934).
- E. Heuser. Textbook of Cellulose Chemistry. McGraw-Hill Book Co. New York (1924).
- Henry Gilman. Organic Chemistry. John Wiley & Sons. New York (1938).
- H. Levinstein. Cellulose acetate. Its manufacture and applications. E. Bean, Ltd., London (1932).
- H. A. Levev. Which cellulose derivative? A series of simple physical and chemical tests. Chemical Industry (New York) 36, 423-6 (1935).
- Fritz Ohl. Cellulose acetate foils. Kunstseide 14, 146-50 (1932).

- S. P. Palmer. The uses of cellulose acetate. Plastic Products 10, 58 (1934).
- K. Roos, H. Friese. Cellulose acetate. Kunstseide 11, 455 (1929).
- A. V. Schutter. Transparent cellulose films. Kunstseide 15, 158-63 (1933).
- E. C. Worden. The technology of cellulose esters. D. Van Nostrand Co., New York, 1916, vols. 1 (5 pts.) and 8.

Rubber Hydrochloride

- Anonymous. Goodyear Pliofilm. India Rubber World 91, 35 (1935).
- Anonymous. Chemical derivatives of rubber. India Rubber World, 92, 52 (1935).
- A. B. Clunan. Pliofilm as a packaging material. India Rubber World 98, 46-7 (1938).
- C. Ellis. The chemistry of synthetic resins. Reinhold Publishing Corp., New York, 1935, vol. 2.
- H. I. Waterman, C. G. H. Max, J. J. Leenderste. Preparation from rubber of plastic materials for the manufacture of films and threads. Chem. Weekblad 31, 614 (1934).
- K. Memmler. The Science of Rubber. Reinhold Publishing Corp., New York, 1934.